

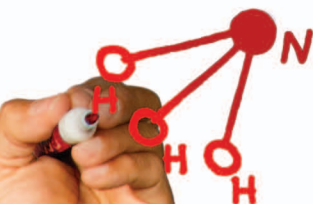
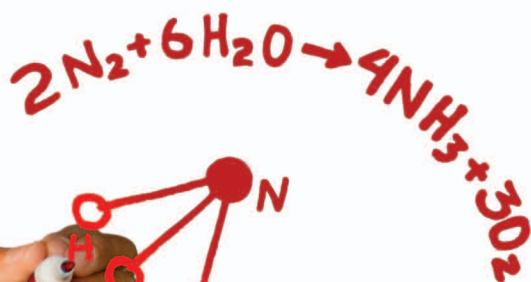


ENERGY

FOR A RAINY DAY

Los Alamos materials scientist Fernando Garzon has a plan for national-scale renewable-energy storage



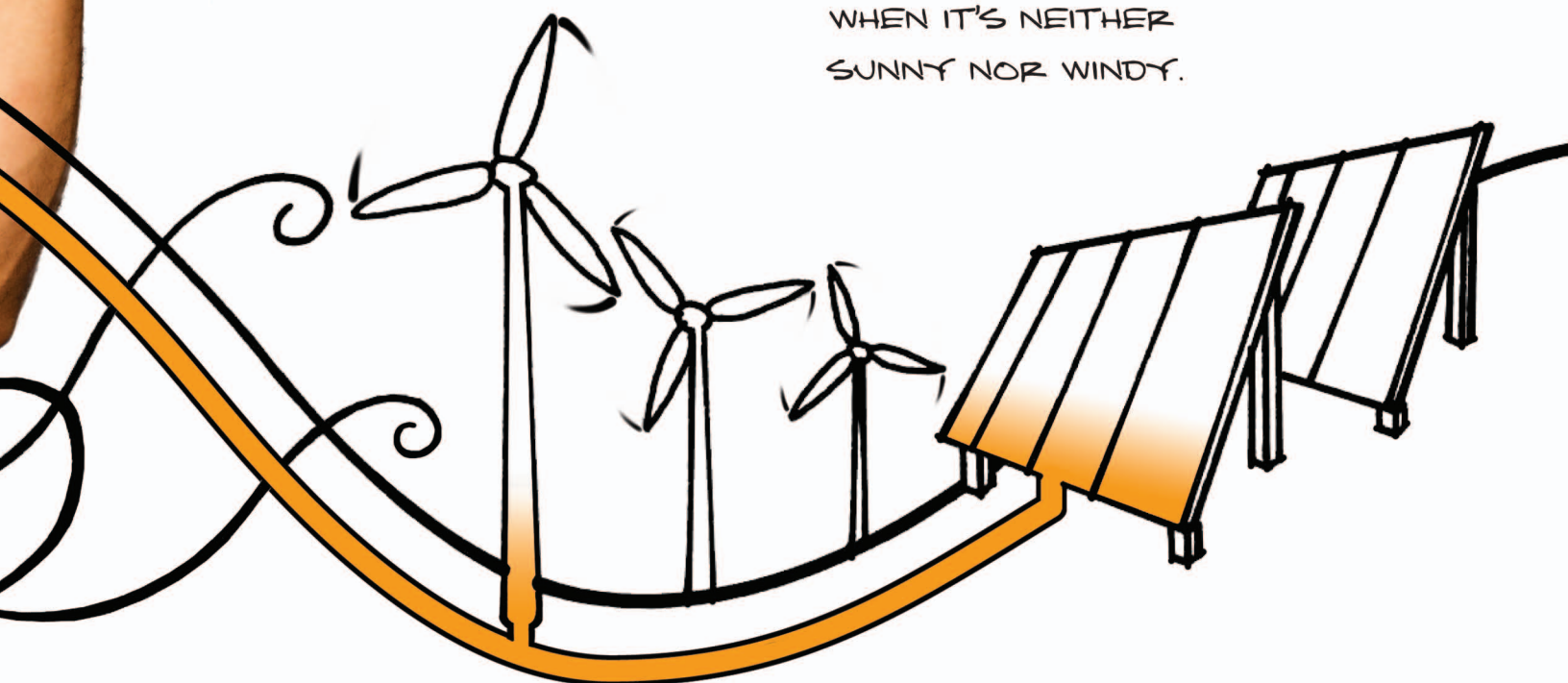


Los Alamos is pioneering technology

TO STORE
SOLAR AND WIND ENERGY
IN READY-TO-USE,
HIGH-CAPACITY CHEMICAL BONDS

**so that the juice
keeps flowing**

WHEN IT'S NEITHER
SUNNY NOR WINDY.



THE ENERGY AVAILABLE from solar and wind resources in the United States vastly exceeds current needs. Yet both sources suffer from the same deficiency, hindering their development for large-scale use: they are intermittent. They only lead to power generation when the Sun is shining or the wind is blowing. That means extra energy, exceeding the current demand, must be collected whenever the Sun and wind are available, and the excess must be stored in a manner that's easy to access when they're not. However, while available solar and wind resources dwarf the nation's energy demand, the U.S. energy storage capacity doesn't come close to meeting the energy demand.

The current electrical grid doesn't rely much on energy storage. Rather, when demand increases or decreases in one part of the grid, regional fossil fuel-based plants either adjust their fuel burn accordingly or exchange power with other parts of the grid. However, because utilities can't turn on additional power generation units as quickly as the demand can increase, readily available additional power comes with a cost: Either regular gas turbine-generator systems must run all the time at low power, essentially idling until they need to be cranked up, or special, fast-startup systems must be brought online. Both options are inefficient, consuming more fuel per kilowatt of electricity than normal operations.

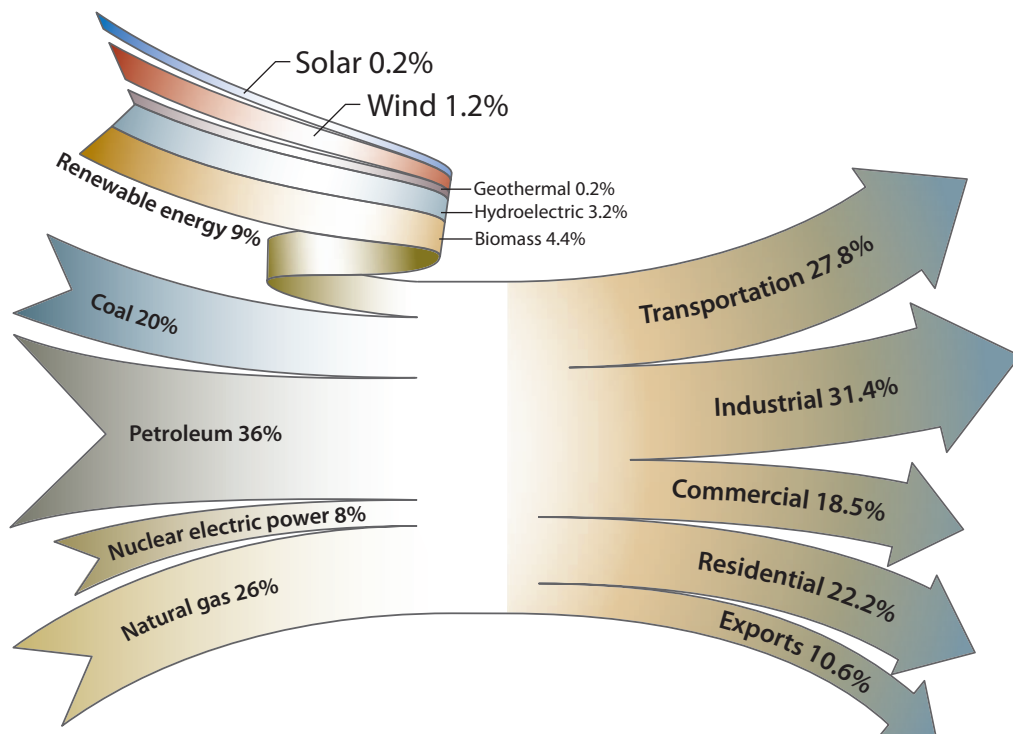
This inefficiency could be mitigated if there were adequate energy storage available. Additional turbines could run at optimal efficiency levels, producing more energy than needed and storing the excess for later. But current energy storage technologies fall short. Batteries, for example, have far too little energy density to meet power plant-scale needs,

much less grid-scale needs. They are also expensive, slow to charge and discharge, and too limited in operating life to meet the storage requirements for everyday demand-matching activity. And significantly increasing the nation's wind and solar capacity would necessitate dramatically exceeding those storage requirements.

Fuel from air

Making the power supply reliable, despite unpredictable demand, is known as firming. Firming fossil fuel-based power is relatively straightforward (although inefficient), but firming wind and solar is much more difficult. The amount of power extracted by a wind turbine, for example, is proportional to the cube of the wind speed, so if the wind speed drops in half, the power produced drops to one-eighth of its previous level. Only extremely high-capacity and rapidly accessible energy stores can accommodate such large and sudden decreases in power production. And only chemical bonds, which can store energy at a density about 100 times greater than that of batteries, have the potential to meet those needs—kicking in enough power on a moment's notice to replace the seven-eighths that was just lost.

Fernando Garzon, a materials scientist at Los Alamos, has a plan to store energy on a national-use scale in the chemical bonds of an unlikely molecule, ammonia. While chemical energy today is largely synonymous with carbon-based fuels, ammonia (NH_3) is nitrogen-based. Garzon's plan is to rapidly convert large quantities of electrical energy into this carbon-free fuel supply, and then convert it back to electricity as needed.



According to the U.S. Energy Information Administration, the total American energy consumption, in all forms, is the equivalent of approximately 10.5 kilowatts of continuous electricity use per person. That's more than four times the global average and enough to power 175 incandescent, 60-watt light bulbs on an ongoing basis. About 4.9 percent of that energy derives from noncombustible, renewable sources, and, of those, hydroelectric and geothermal energy contribute more than two-thirds. The most intermittent sources, wind and solar, amount to only 1.2 and 0.2 percent of U.S. consumption, respectively. It will take a new approach to energy storage to substantially increase the contribution from wind and solar.

Ammonia storage tanks will need to crop up all over the United States if ammonia-based energy storage is to enable large-scale domestic solar and wind power. Onsite conversion facilities will use the incoming renewable-sourced electricity to create ammonia and then re-convert the ammonia into electricity as dictated by the energy demand.



“Nitrogen is abundant and it’s free,” Garzon says. “It makes up 80 percent of the air we breathe and, as an energy storage medium [ammonia], is completely free of pollution.” The nitrogen for Garzon’s process would indeed come from the air and would ultimately be returned to the air once the stored energy is converted back into electricity. The only other raw ingredient consumed in the process is water, and that, too, is restored in the end.

The idea works like this: Electricity is generated by wind and solar farms whenever wind and sunlight are available. The electricity that exceeds the current demand is redirected into Garzon’s electrochemical conversion system, where it is used to isolate the atoms that go into ammonia—nitrogen from the air and hydrogen from the electrolysis of water (separation of H_2O into H_2 and O_2). Both nitrogen and hydrogen are initially supplied in the form of diatomic molecules (N_2 and H_2), but they must be separated into individual N and H atoms with help from a metal catalyst before they can be combined into ammonia. The details of this conversion, including operating temperatures and pressures, quantities of nitrogen and hydrogen, and selection of catalysts and other facilitating materials, are currently being researched.

Once the ammonia has been created, it enters a large storage tank to await the renewable-energy equivalent of a rainy day. When energy is needed, the ammonia is fed into a fuel cell where it is readily converted back into nitrogen, water, and electricity. Such ammonia-fueled fuel cells already exist and are both highly efficient and fully scalable. They go on and off easily and support a large flow of electricity. And they do not require inefficient fossil-fuel firming.

Ammonia also has the advantage of being portable. Because ammonia is easily liquefied, it is convenient to transport and store. There may ultimately be many thousands

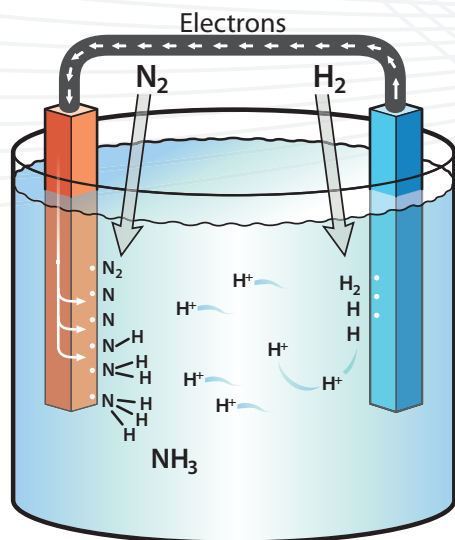
of such tanks around the country, potentially connected by tanker truck routes or pipelines—as well as power lines.

So what’s the X factor in Garzon’s idea? It’s the chemical bonds themselves. The energy storage capacity of nitrogen’s bonds is both the plan’s greatest virtue and its biggest dilemma: current methods for cleaving diatomic nitrogen’s triple bond to make individual nitrogen atoms, $\text{N}_2 \rightarrow \text{N} + \text{N}$, require a great deal of energy. Some of that energy is recovered when the process is reversed in the fuel cell, but it still presents a large hurdle along the way.

Relieving the pressure

An industrial-use version of this conversion process, including the N_2 separation, already exists. It is widely used to manufacture ammonia for agricultural and other applications, but, until Garzon and others improve upon it, it’s far too expensive for firming renewable energy. Known as the Haber-Bosch process, it relies on high-pressure catalysis: the diatomic gases N_2 and H_2 flow over a catalytic surface made from either iron or ruthenium, which breaks the diatomic bonds, creating individual nitrogen and hydrogen atoms. These atoms then combine to form ammonia gas, NH_3 .

Sounds good, but here’s the problem: The rate-limiting step, not surprisingly, is breaking the diatomic nitrogen molecule’s triple bond. In order to obtain a decent reaction rate and adequate performance from the catalysts, the process must be run at a high temperature, around 500°C . But the ammonia-building reactions are exothermic, and a high temperature suppresses them by inhibiting the release of heat. This would be a deal-breaker, except that, because the overall reaction merges reactants together, there are more incoming molecules (N_2 and H_2) than outgoing molecules (only NH_3). As a result, the reaction can be driven in the desired direction



Garzon's electrochemical process will use incoming solar- and wind-produced electricity to convert nitrogen (from the air) and hydrogen (from the electrolysis of water) into ammonia. Electrodes coated with specialty materials (shown as red and blue bars) catalyze the separation of diatomic nitrogen and hydrogen molecules into individual atoms. Positively charged hydrogen ions produced at one electrode travel through an electrolyte material (shown as liquid) to the opposite electrode, where the nitrogen atoms are produced. Electrons from the hydrogen atoms flow to the nitrogen electrode through an external wire. At the nitrogen electrode, hydrogen attaches to nitrogen to make ammonia, which is then released and subsequently harvested. To make the process sufficiently energy-efficient to meet grid-scale energy storage requirements, both the electrode and the electrolyte materials need to be carefully engineered at the molecular level.

by imposing a very high pressure: the system essentially seeks to relieve its pressure by reducing the number of reactant molecules present, thereby favoring the production of ammonia. Unfortunately, the amount of pressure required to accomplish this is enormous, around 200 atmospheres, and with that much pressure comes tremendous expense in terms of reinforced reaction vessels and pipes, energy-consuming pumps and compressors, and heightened safety accommodations.

The solution, then, is to invent a way to make this process work at low temperatures and low pressures. This is a materials science challenge because there are two main components to the electrochemical conversion system, and both will require new, specialty materials to do their jobs under less extreme conditions. The two components are the electrodes, where the catalyst does its work, and the electrolyte that lies between them.

Electrodes and electrolytes

First and foremost, a new electrode material will need to do the heavy lifting, breaking the strong triple bond in diatomic nitrogen from the air. The current Haber-Bosch process uses heat and pressure to drive the breaking of N_2 bonds on the iron and ruthenium surfaces. The new Los Alamos process, however, will use electrical energy from wind and solar farms to facilitate cleaving the diatomic bonds, so the reactions can occur at lower pressures and temperatures.

Garzon has a lead on a novel material that might do the trick: molybdenum nitride. Early experimentation with molybdenum nitride surfaces has proven to be promising, splitting diatomic nitrogen and producing intermediate structures along the way to producing ammonia, NH and NH_2 , attached to molybdenum on the electrode surface.

These successes were first revealed in neutron scattering experiments carried out by Garzon's colleagues Tony Burrell, Alex Mueller, and T. Mark McCleskey at the Los Alamos Neutron Science Center.

In addition, techniques developed at Los Alamos allow the molybdenum nitride to be built into a nanostructured material capable of providing an enormous surface area for catalysis from a very small amount of the catalyst itself: an incredible 70 square meters per gram of molybdenum nitride. Because the surface is textured at the nanoscale, the large surface area is achieved without an especially large electrode. This is an important achievement because the greater the surface area, the greater the reaction throughput. The research team has also developed a thin-film deposition technique to produce large-surface-area films on supporting electrode structures.

The new nitrogen-to-ammonia conversion process will also require a new electrolyte to convey hydrogen from one electrode (where hydrogen atoms are isolated) to the other (where they combine with nitrogen to make ammonia). The electrolyte can't be water or water-based, like the acid solutions used in some batteries, because water prevents the catalysts from functioning. And it needs to selectively transport positively charged hydrogen ions—otherwise known as protons—but reject electrons, forcing the electrons along an external wire to the other electrode. (Although the electrons must ultimately arrive at the same nitrogen-binding electrode as the protons to prevent an overall charge buildup, they get there by a different road.)

Garzon believes he and his team have found two viable classes of electrolytes to do this job: one liquid and one solid. The former, ionic liquids, are salts that liquefy at or below room temperature. They exhibit excellent chemical

stability and dissolve ammonia as well as water does, and they are compatible with the catalysts under consideration. They also offer great potential to be specifically tailored to support nitrogen conversion into ammonia with maximum proton conductivity. However, they are relatively untested. Los Alamos materials chemist James Boncella is working with Garzon to better understand how ionic liquids work and how they can be improved as electrolytes.

The other possibility is a solid proton conductor. This would take the form of a relatively thin polymer or ceramic strip sandwiched between the two electrodes. The optimal material will no doubt bear a complex molecular structure that was carefully designed for the purpose of proton conduction. However, the common chemical tin pyrophosphate (an ingredient in toothpaste) has already been shown to work to a limited extent, proving the potential of solid proton conductors.

The overall electrochemistry of both solid proton conductors and ionic liquids is not yet well known (as the electrochemistry of water is), making necessary additional foundational research by Garzon's team. For example, Neil Henson, another Los Alamos materials chemist, performs detailed theoretical modeling of the molecular structures

of ceramic electrolytes, to help figure out how they transport protons, and molybdenum nitride electrodes, to help figure out how they separate diatomic nitrogen and synthesize ammonia.

In fact, the materials science solutions for both the electrolyte and the electrodes will require significant research and experimentation. The Los Alamos scientists need to create theoretical models of how the materials function at the molecular level. They need to synthesize each material under consideration and test its performance by measuring quantities such as ion formation, ammonia solubility, proton transport, and surface reaction rates. No question, these scientists have their work cut out for them.

It remains to be seen whether the new and improved, ammonia-producing electrochemical conversion process, including the N_2 separation, can be done in a practical, low-cost, and large-scale way. But Garzon feels that he and his colleagues at Los Alamos have already demonstrated the validity of the concept.

"Technologically, yes, I believe it will work," Garzon says. "In my mind, the greater uncertainties are economic and political—whether or not our design will become a national infrastructure to support renewable energy." **LDRD**

—Craig Tyler

New Day for Nitrogen

If Garzon and his team are successful, they will do more than firm up renewable sources of energy; they will also dramatically cut costs in a major segment of the chemical industry.

Ammonia production today is big business. Approximately 200 million metric tons of ammonia are produced worldwide each year, and more than one percent of all energy produced globally is consumed in its production. About five-sixths of this ammonia is used in fertilizers; the rest has a variety of uses including cleaning products, nutrients for fermentation processes, and antimicrobial agents for animal feeds and beef, to name a few. Ammonia is also the starting point in the manufacture of nearly all nitrogen-based compounds, supporting a wide range of applications that includes propellants and explosives. Ammonia

can even be used as a clean-burning combustion fuel; it has been successfully demonstrated in automobiles and aircraft rocket engines, although it contains only about 40 percent as much energy as an equivalent volume of gasoline.

"The way I see it unfolding," Garzon says, "this technology will be introduced into the ammonia industry initially, benefitting fertilizer production and maybe lowering food prices. Then there will be a regional-scale energy storage test somewhere, using ammonia conversion, storage, and fuel cells to firm up a local energy utility's wind or solar production. If that proves successful, then hopefully our work will accelerate the use of wind and solar power nationally."

